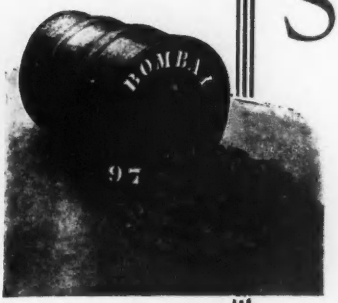
691.3
CEM

CEMENT AND LIME MANUFACTURE

XIV. No. 2 FEBRUARY 1941 PRICE 1/- MONTHLY



"SLUGOIDS"

Regd. No. 532240.

A perfect substitute for small size forged steel balls at less than half the cost.

SLUGOIDS are made of Rolled High Carbon Steel of special analysis and are of EQUAL LENGTH WITH DIAMETER. While they can be supplied just as cut from the special Steel Bars the HEAT-TREATED SLUGOIDS are to be recommended. The patent Heat-treatment process imparts a degree of Hardness not otherwise obtainable: Brinell Hardness No. 512 approx.

Write for Samples and Prices

HELIPEBS LTD.

GLOUCESTER · ENGLAND

LIBRARY
UNIVERSITY OF WASHINGTON
MAR 27 1941
SEATTLE, WASHINGTON

PUBLISHED BY CONCRETE PUBLICATIONS LTD., 14, DARTMOUTH STREET, LONDON, S.W.1.

The CHIEF CHEMIST of one of the largest English Cement Manufacturers writes :

"I must offer my congratulations on the excellence of 'The Cement Chemists' and Works Managers' Handbook.' I feel sure it will prove essential to those for whom it is intended."

"CEMENT CHEMISTS' AND WORKS MANAGERS' HANDBOOK"

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

186 pages, 152 tables, 14 illustrations. Published 1940.
Price 15s.; by post 15s. 7d. inland, 15s. 8d. abroad.

GIVES in handy form all the data used in the manufacture, chemistry, and testing of cement. An indispensable work of everyday reference. Saves time and labour, and ensures accuracy.

Comparison in tabular form of the cement specifications of 33 countries; Dimensions of various standard sieves; Weights and volumes of slurry; Capacities of tanks and kilns; Gas volumes per ton of clinker; Kiln data; Fan horse-power; Volumes and weights of gases from kilns; Density of exit gases; Density of gases in kilns; Proportioning and chemical control of raw mixes; Heat balance.

Conversion tables (English-metric and metric-English)—Pressures, density and concentration, heat, work, energy, calorific values, specific surface, air passing through pipes, rate of flow.

Physical tables.—Properties of substances, compounds, and alloys; Solubilities of gases in water; Specific gravities of hydrochloric, sulphuric and nitric acids at 15 deg. C.; Connection between specific gravity, degrees Twaddell and degrees Baume; Conversion of hydrometer readings to specific gravity; Weights of substances; Tension of aqueous vapour; Density and volume of water at different temperatures; Weights of sheet metal; Weights of water vapour and dry air in saturated air at different temperatures; Calibration of pyrometers; Heat units; Combustion data; Freezing mixtures; Evaporative power, calorific power and carbon value.

Standard solutions and bench reagents; Chemical tables (atomic weights, gravimetric factors, conversion of weights of precipitates).

Chemical analysis (Argillaceous and calcareous materials, coal and coke, gypsum, cement).

Testing of cement (Setting time, consistency, fineness, soundness, tensile strength).

PUBLISHED BY

CONCRETE PUBLICATIONS LIMITED

14, DARTMOUTH STREET, LONDON, S.W.1

CEMENT AND LIME MANUFACTURE

PUBLISHED 20TH OF EACH MONTH. PRICE 1/- A COPY. ANNUAL SUBSCRIPTION 12/- POST FREE

PUBLISHED BY
CONCRETE PUBLICATIONS LIMITED
14 DARTMOUTH STREET, LONDON, S.W.1

TELEPHONE: WHITEHALL 4581.
TELEGRAPHIC ADDRESS:
CONCRETIUS, PARL, LONDON

PUBLISHERS OF
"CONCRETE & CONSTRUCTIONAL ENGINEERING"
"CONCRETE BUILDING & CONCRETE PRODUCTS"
"CEMENT & LIME MANUFACTURE"
"THE CONCRETE YEAR BOOK"
"CONCRETE SERIES" BOOKS, ETC.

VOLUME XIV. NUMBER 2 FEBRUARY 1941

Control of Rotary Kilns.

THE following is an abstract of a discussion on the control of burning operations in the manufacture of Portland cement, published in the "Cement Mill" section of our United States contemporary "Concrete" (November, 1940).

An interesting example of modern kiln control was observed recently in a large cement plant in the Mississippi Valley. Each of the kilns was fitted with an "electric eye," composed of a photo-electric cell at the kiln which was connected with the interior of the kiln through the agency of thermo-couples. About 40 ft. away the temperature was recorded automatically by an indicator on a slowly moving sheet of paper.

It is estimated that in a kiln 200 ft. long the raw material occupies about 2½ hours in passing through from the feed end to the point of discharge of the clinker. According to Lea and Desch, in "The Chemistry of Cement and Concrete," the reactions which usually occur during this process may be roughly classified as follows: (1) Evaporation of free water; (2) Release of the combined water from the clay; (3) Dissociation of magnesium carbonate; (4) Dissociation of calcium carbonate; (5) Combination of lime and clay. Evaporation of free water takes place at or below 100 deg. C., but the release of the water that is combined in compounds composing the clay only becomes appreciable at about 500 deg. C. The change that occurs in the clay when it loses its combined water is a subject on which there is much disagreement; no doubt the reactions that take place are influenced to a considerable extent by the original composition of the clay. The dissociation of magnesium carbonate occurs at relatively low temperatures. The pressure of the released carbon dioxide reaches atmospheric pressure at 402 deg. C., although the decomposition pressure of calcium carbonate, when heated alone, does not reach atmospheric pressure until a temperature of about 900 deg. C. has been reached.

In mixtures of calcium carbonate and finely-divided quartz reaction occurs very faintly at a temperature as low as 600 deg. C., then proceeds very slowly up to about 800 deg. C., reaches an appreciable speed at 1,100 deg. C., and a rapid speed at 1,400 deg. C. Messrs. Lea and Desch state that monocalcium silicate is the first of the clinker compounds to be formed, regardless of the ratio of lime to silica in the mixture. But the monocalcium form is fairly readily converted to dicalcium silicate, and, in mixtures of sufficient lime content, all of the combined silica is present as dicalcium silicate ($2CaO.SiO_2$) by the time a temperature of 1,200 deg. C. has been reached. Formation of tricalcium silicate ($3CaO.SiO_2$) proceeds very slowly at a temperature even as high as 1,500 deg. C., but the addition of alumina and ferric oxide to the lime-silica mixture causes a marked increase in the rate of its production. In no case, however, is the formation of tricalcium silicate likely to be started until a temperature of 1,300 deg. C. has been reached.

The measurement of flame and clinker temperatures is accomplished in several ways. The use of a photo-electric cell has already been mentioned. Another method involves the use of an optical pyrometer. Actual flame temperatures within the kiln have been reported as ranging from 1,340 to 1,560 deg. C. It is, however, difficult to estimate the accuracy of temperatures so reported. Another point of importance is the time occupied by the contents of a rotary kiln in passing through the clinkering zone—the portion of the rotary kiln in which the temperature is at the maximum value. Some investigators give the period of 20 minutes as an estimate of the average time required by the contents of the kiln to pass through the clinkering zone.

The temperature of the clinker at the moment of its discharge from the kiln is likewise a matter that has given rise to many differences of opinion; and in all probability, if it were possible to determine the actual value, much variation would be found with different kilns and different raw materials. Investigators seem to agree on the range from 1,000 deg. C. to 1,300 deg. C. (1,830 to 2,340 deg. F.) as covering this temperature in most cases. The actual formation of the clinker within the kiln is said to occur at the time when the so-called exothermic reaction in the raw mix takes place—when the temperature rises rapidly from around 1,100 deg. C. to 1,200 deg. C. to between 1,300 deg. C. and 1,350 deg. C.

Improvement in kiln production does not always depend upon the process of taking out old installations and putting in new kilns. In one instance the quantity and quality of the output were improved by an installation by means of which all primary air of combustion is passed through a fan installed in a housing in which the temperature is kept at not less than 600 deg. F. This pre-heating of the primary air of combustion results in a saving in kiln fuel. After this device was installed the production of clinker averaged 1,600 barrels per day for each 10-ft. by 150-ft. kiln.

A device that has aided in the control of rotary kilns is a variable-pitch speed changer that provides the necessary flexibility in speed transmission without the necessity for the use of variable-speed motors.

The Influence of Fluxes on the Burning of Cement.

IN an interesting series of articles published in *Rock Products* for May, June and July, 1940, Mr. Steven Gottlieb (chief chemist of the Portland Cement Co. "Nesher," Ltd., of Haifa, Palestine) describes his experience in the use of fluxes. The following is an abstract of these articles.

The effect on the formation of clinker constituents in burning due to changes in the chemical composition are well known from the studies of the quaternary system(1) CaO-SiO_2-Al_2O_3-Fe_2O_3 and the systems subsequently formed at higher temperatures, CaO-$2CaO.SiO_2$-$5CaO.3Al_2O_3$-$4CaO.Al_2O_3.Fe_2O_3$, etc. Recent research(2) also adds much to our knowledge of the part played by the alkalis. We cannot, then, be said to be ignorant of the influence of chemical composition on the formation of the clinker constituents at different burning temperatures.(3)

Chemical reactions between solid substances, even when they are very intimately mixed, tend to proceed slowly. When heated to higher temperatures, a stage must be reached at which the atom or molecule groups increase the speed of their movements to such an extent that they are capable of "interchanging," i.e., they oscillate so strongly around their lattice points that a great number of them change places.(4) With silicates, a considerably greater rigidity of the lattice-structure must be overcome than in the case of most other substances, in order to achieve this greater activity. According to latest experience,(5) however, that rigidity is not equal in all places, the lattice-structure being interspersed with numerous sub-microscopic faults ("lattice wounds"). The ions found in such faulty places are less fixed than the inner ones of the crystal, and therefore are subject to greater reactivity.

By the application of suitable fluxes it is possible to diminish the reaction inertia of silicates even at the short heating and cooling times of practice, and thus to approach the state of equilibrium. The structure of a highly polymerised lattice (e.g. in the glassy state) can be loosened by flux, resulting in greater reactivity. Thus the formation of $3CaO.SiO_2$ at above 2,400 deg. F. can be greatly accelerated by adding CaF_2 to the raw mix. $MgSiF_6$ operates in a similar way.(6) The fluxes act in these cases as mineralisers, the fluxes with small ions carrying high electric charges being the most active. The fluorine ion disintegrates the complex SiF_4 ion. The SiO_4 and SiF_4 ions brought about by such decomposition interchange to form a homogeneous equilibrium, in nearly the same way as in a number of heterogeneous catalytic processes.(7) Fluorides exercise a mineralising influence on aluminate systems, just as in the case of silicate systems.(8)

Admixtures of Fe_2O_3 and Al_2O_3 are often used to lower the silica modulus of the raw material, and are frequently added even to raw mixes that have chemical compositions quite perfect without them, with a view to improving yield, heat economy, and quality of production in the case of raw materials "difficult to burn."(9) The use of the term "difficult to burn," which suggests to most cement makers a well-known peculiarity of some raw materials, proves

that Fe_2O_3 and Al_2O_3 as fluxes can show various results dependent on the physico-chemical state of the raw materials and the kiln system adopted.

Experience with Modern Shaft Kilns.

In two plants belonging to the same concern, up-to-date automatic shaft kilns were in operation. For some time the modern rotary kiln had seemingly supplanted the automatic shaft kiln. Recently the latter has undergone such a remarkable improvement that to-day it can be considered an automatic burning machine on a par with the rotary kiln. The raw mix is pneumatically blended to any desired chemical composition, then mixed with the necessary quantity of coke or anthracite dust and water and pressed into small briquettes. Feeding the kiln with briquettes and discharging the clinker through the rotary grate are done entirely automatically and can be electrically regulated from the kiln floor, where combustion air is equally controllable.

The kilns in both plants were fired with the same fuel (12,600 B.T.U. coke was used). Burning and yield, however, were quite different. In plant No. 1 there were no difficulties in burning the raw mix, production went on smoothly, heat consumption and capacity being very favourable, and the clinker of high quality. In plant No. 2 the results were less successful. Losses in edge fire, flaws in the middle, etc., frequently occurred, and heat consumption and kiln output were unfavourable. Considerable quantities of insufficiently burned clinker were produced. Milling and blending of raw mix, the admixture of coke, checking, etc., were carried out in an identical manner in both plants, so that the composition of the raw mix and briquettes could not be responsible for the difference in the two plants. This difference can therefore only be due to the various properties of the individual raw materials of which the raw mixes were composed. Plant No. 1 used soft marl of a very hygroscopic nature in which the water content fluctuated between 15 and 20 per cent. according to the humidity. The raw mix was obtained by mixing high and low calciferous marls. The raw material of plant No. 2 consisted of shale and hard limestone rock in which lumps of SiO_2 were interspersed. It was possible to keep the raw mix in both plants at the same chemical composition.

The drying of raw materials in plant No. 1 consumed more heat due to high moisture, whereas raw grinding in plant No. 2 was more expensive, so that preparation of practically equally fine raw mixes involved nearly the same expenditure. The water consumption of the 2-in. diameter briquettes with which the kilns were fed amounted to 16 per cent. and 11·5 per cent. in plants No. 1 and No. 2 respectively. In spite of the greater amount of water to be evaporated in plant No. 1, the heat required for burning was less than in plant No. 2, the kilns at the same time working at a higher capacity, more uniformly and at a lower fuel consumption (*Table* 1). Although experiments in grinding a finer raw mix in plant No. 2 caused an increase in water consumption of as much as 18 per cent. for the briquettes, the plasticity nevertheless became worse and burning was rendered still more difficult.

For the purpose of increasing the capacity in plant No. 2, CaF_2 was first tried as a flux. In conformity with theoretical expectations burning was much easier, fuel consumption decreased, and burning became more uniform. Strength, particularly compressive strength, was considerably increased. A feature of the setting time of this CaF_2 cement was that it sometimes showed flash set, with the final set greatly retarded. The heat evolution during the hardening process (which was measured in a Dewar vacuum vessel, 300 grams of cement and 75 grams of water being used) showed by the delayed temperature maxima the

TABLE 1.—PROPERTIES OF CEMENTS GROUND IN COMPOUND MILLS OF THE SAME TYPE (EACH WITH 5 COMPARTMENTS) WITH THE ADDITION OF 4 PER CENT. GYPSUM

	PLANT No. 1		PLANT No. 2	
	Raw Mix (Percentages)	Clinker (Percentages)	Raw Mix (Percentages)	Clinker (Percentages)
Residue on Sieve No. 72 (>200μ)	0.8	....	0.4	....
" " " " 170 (>88μ)	19.0	....	16.0	....
SiO_2	13.10	21.62	13.65	21.64
Al_2O_3	4.00	6.94	3.99	6.80
Fe_2O_3	1.52	2.65	1.67	2.88
CaO	43.71	67.10	44.90	66.30
MgO	0.70	1.08	0.50	0.70
SO_3	Traces	0.16	Traces	Traces
Alkalies	0.12	0.21	0.10	Traces
Ignition loss	36.80	0.20	35.20	1.60
Free lime	....	0.35	....	2.90

	Plant No. 1	Plant No. 2
Fineness: Weight per litre	980 gr.	950 gr.
Residue on Sieve No. 72 >210μ	0	0
" " " No. 170 > 88μ	5 percent	4.5 percent
" " " No. 240 > 65μ	12 "	9.8 "
Setting time: Water used for plastic consistency	26 "	27.5 "
Initial setting at 65 deg. F.	2 hr.	1 hr. 20 min.
Final " " "	3 hr.	3 hr.
Soundness: Lechatelier test	0 mm.	5 mm.
Tensile strength (mortar with 8 percent water) After 1 day at 65 deg. F.	227 lb./in.^{2}	212 lb./in.^{2}
" 3 days	420 "	294 "
" 7 "	483 "	345 "
Crushing strength (mortar with 8 percent water) After 1 day at 65 deg. F.	1700 "	852 "
" 3 days	4960 "	2990 "
" 7 "	6245 "	4405 "

15.2 percent coke (clinker) used; output per kiln 700 bbl./24 hr. in plant No. 1
20.6 percent coke (clinker) used; output per kiln 500 bbl./24 hr. in plant No. 2

peculiarity of this cement which was also noticed in its setting time. It was remarkable that the delay in the setting time was greater when the clinker was sharply burned and the strengths were somewhat lower in comparison with the clinkers burned at medium temperatures (about 2,500 deg. F.). The clinkers, even when cooled rather fast, showed a good deal of dusting (i.e. " crumbling ").

It is possible that CaF_2 as a mineraliser also decomposes $3CaO.SiO_2$ far below its decomposition temperature at a noticeable rate.

Later on, low-grade bauxite with an Al_2O_3 content of about 30 per cent. was tested as a flux in plant No. 2. Burning became more uniform, but was far from satisfactory. Fuel consumption could not be lowered, but the quality of the clinker improved. Very good results, however, were achieved with iron oxide. The fuel consumption equalled that of plant No. 1, burning became easy, and the capacity was considerably increased. Cement properties and heat evolution curves are shown in *Table* 2 and *Fig.* 1.

TABLE 2.—AVERAGE RESULTS OBTAINED BY ADDING FLUXES TO THE RAW MIX IN PLANT NO. 2.

	1 percent CaF_2 medium burned	1 percent CaF_2 strongly burned	1 percent bauxite	1 percent Fe_2O_3
Fineness: Weight per litre	940 gr.	960 gr.	975 gr.	960 gr.
Residue on Sieve No. 72 >210μ	0 percent	0 percent	0.1 percent	0 percent
Residue on Sieve No. 170 >88μ	3.8 "	4.0 "	4.2 "	4.0 "
Residue on Sieve No. 240 >65μ	10.0 "	10.0 "	13.0 "	11.0 "
Setting time: Water used for plastic consistency	27.5 "	27.5 "	26.8 "	26.5 "
Initial set at 65 deg. F.	4 hr.	1 hr.	2 hr.	2 hr.
Final " " " "	7 "	8 hr. 30 min.	3 hr.	3 hr. 30 min.
Soundness: Lechatelier test	0.5 mm.	1.5 mm.	0.5 mm.	0.5 mm.
Tensile strength (mortar with 8 percent water) After 1 day at 65 deg. F.	184 lb./in.²	170 lb./in.²	285 lb./in.²	220 lb./in.²
" 3 days	400 "	327 "	400 "	391 "
" 7 "	512 "	370 "	450 "	495 "
Crushing strength (mortar with 8 percent water) After 1 day at 65 deg. F.	566 "	568 "	1550 "	1100 "
" 3 days	5540 "	3550 "	4400 "	4160 "
" 7 "	6970 "	4410 "	5700 "	5750 "
	17.4% Coke/Clinker; one kiln 617 bbl./24 hr.	19.8% Coke/Clinker; one kiln 587 bbl./24 hr.	20% Coke/Clinker; per kiln 575 bbl./24 hr.	15.3% Coke/Clinker; per kiln 675 bbl./24 hr.

To test the behaviour of the raw mix with the addition of fluxes in plant No. 1, an experiment was made with the same iron oxide as was used in plant No. 2. Thus the possibility was provided of comparing the raw mixes of both plants again at the same chemical composition but at lower alumina modulus. Iron oxide admixture, however, proved a failure in plant No. 1, although the fuel consumption was still reduced. Burning became exceedingly difficult; the mixture tended to adhere to the firebrick lining and cement strength was lower than when it was burned without iron oxide. On the other hand plant No. 1 reacted favourably to 1 per cent. of bauxite as a flux. Fuel consumption was lowered 5 per cent. and early strength and heat evolution during hardening were

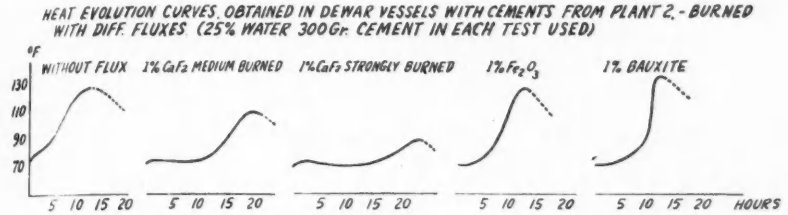


Fig. 1.

getting higher (*Table* 3). However, on account of the chemical resistance against aggressive solutions, especially sulphates, it was not thought advisable to increase the alumina modulus.

This example shows that reports with different results about the behaviour of iron oxide, alumina, bauxite, etc., may not be contradictory. The effect of different fluxes depends on the chemical composition, the physico-chemical properties of the raw constituents, and other local circumstances.

Shaft and Rotary Kilns.

After a number of years of practical experience, a series of comparative tests was carried out for the purpose of obtaining specific data on fluxes. These tests were carried out in an oil-fired laboratory furnace and a complete study was made of the degree and rate of combination by using different raw materials.

TABLE 3.—AVERAGE RESULTS OBTAINED BY ADDING FLUXES TO THE RAW MIX IN PLANT NO. 1.

	Without any addition	1 percent Fe_2O_3	1 percent bauxite
Fineness: Weight per litre	980 gr.	975 gr.	990 gr.
Residue on Sieve No. 72 >210μ	0 percent	0 percent	0.2 percent
" " " " 170 > 88μ	5 "	4.8 "	5 "
" " " " 240 > 65μ	12 "	11.6 "	12.2 "
Setting time: Water used for plastic consistency	26 "	25.8 "	26.2 "
Initial set at 65 deg. F.	2 hr.	2 hr. 10 min.	1 hr. 50 min.
Final " " " "	3 "	3 hr. 20 min.	3 hr. 20 min.
Soundness: Lechatelier test	0 mm.	0 mm.	0 mm.
Tensile strength (mortar with 8 percent water) After 1 day at 65 deg. F.	227 lb./in.^{2}	227 lb./in.^{2}	341 lb./in.^{2}
" 3 days	420 "	415 "	426 "
" 7 "	483 "	472 "	480 "
Crushing strength (mortar with 8 percent water) After 1 day at 65 deg. F.	1700 "	1280 "	2990 "
" 3 days	4960 "	4680 "	4900 "
" 7 "	6245 "	5460 "	5670 "
Constit. compounds of clinkers: $3CaO.SiO_2$	57.5 percent	55.2 percent	55.2 percent
$2CaO.SiO_2$	19.1 "	19.7 "	19.9 "
$3CaO.Al_2O_3$	13.9 "	11.6 "	14.9 "
$4CaO.Al_2O_3.Fe_2O_3$	8.1 "	11.0 "	7.0 "
Free CaO	0.35 "	0.20 "	0.10 "

The furnace was constructed in such a way that, in an inner volume of about 1 cu. ft., it was possible to obtain temperatures up to 2,700 deg. F., and firing could be so regulated that inside this exceptionally large firing space the uniformity of temperature was well maintained. (No greater changes than 10 deg. F. occurred.) The small temperature inaccuracy recorded was negligible because of the way in which the tests were carried out ; namely, three raw mixes were to be compared and about 30 lb. of clinker were to be prepared from each mixture. Thus 140 lb. of raw mix had to be burned and moulded as briquettes of the same size (2 in. by 3 in.). As the capacity of the furnace was only about 15 lb., burning had to be repeated many times to get the necessary quantity of clinker. At each burning equal quantities of all the three raw mixes were put into the furnace, the order of the set briquettes being always changed, thus small differences in temperature

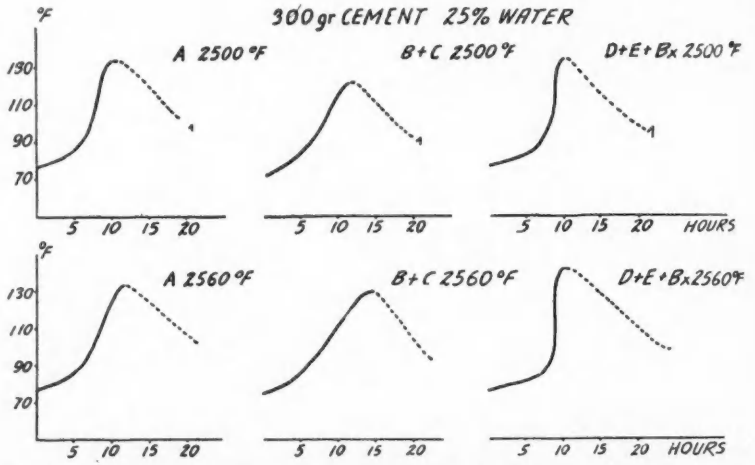


Fig. 2.—Cements Burned from Raw Mixes A, B+C and D+E+Bx at 2500 , and 2560/20. Evolution of Heat during Hardening in Dewar Vessel.

inside the furnace were of no importance for the final sample, which was burned in ten portions or more, mixed together, and ground. Rate of heating, maximum temperature, and cooling were very uniform at each burning (*Fig.* 2). The fuel used had practically no ash content. The bottom slab of the furnace consisted of magnesia firebrick which has shown that it is perfectly non-sensitive against sintering raw mix.[10]

The chemical composition of the raw material constituents to be tested were as shown in *Table* 4. The flint (E) was very closely combined with the chalk in the quarry, consisting of large inclusions between layers of soft chalk (D), the separation of these two constituents proving very difficult. Hard limestone (B) and clay (C) were found in large quantities without impurities. The chemical composition of the argillaceous lime (A) equals the composition of a good cement,

and as this composition was very uniform the lime could be used without any addition.

Experiments with Bauxite.

In the laboratory tests, a raw mix consisting of A and mixtures of the constituents B+C and D+E of the same composition as A were tested. In order to obtain this chemical composition, bauxite with 74 per cent. Al_2O_3 and 20 per cent. Fe_2O_3 had to be added to D+E. The composition and fineness of the test raw mixes were as follows:

Raw mix No. 1	Raw mix No. 2	Raw mix No. 3
100% A	73% B 27% C	86% D 12·6% C 1·4% Bauxite
72% minus 170 mesh	78% minus 170 mesh	78·5% minus 170 mesh

For the purpose of observing the various stages of the clinkering process, all samples were burned at different temperatures, producing in each case about 60 lb. of clinker from all three raw mixes. On reaching the maximum temperature desired at a time, it was maintained for a certain period and then cooled off. To explain the tests, this period is given together with the temperature: that is, $2460_{\ 5}$ means that the maximum temperature of 2460 deg. F. acted for five minutes,

TABLE 4.

	Argillaceous lime (marl) "A"	Hard limestone of pliocene form "B"	Clay "C"	Soft chalk of eocene form "D"	Flint "E"
$CaCO_3$	76.5%	96.2%	18 %	86.2%	38.0%
SiO_2	15.4%	3.2%	51.2 %	16.1%	70.8%
Al_2O_3	3.9%	0.6%	13.2 %	2.2%	0.4%
Fe_2O_3	1.8%	0.5%	6.2 %	1.2%	1.2%
Silica-modulus:	2.6	2.9	2.64	4.7	(40.7)
Alumina-modulus:	2.2	(1.2)	2.11	1.8	(.04)

then it was cooled down at a rate shown in *Fig.* 2. In consequence of the large quantity of clinker burned, grinding could be better controlled and uniform fineness obtained. Clinkers were ground in the laboratory mill under carefully controlled conditions; thus 2,000 sq. cm. per gram specific surface area was uniformly obtained for all clinkers. The results of investigations are shown in *Tables* 5 and 6 and in *Fig.* 3.

From these comparative experimental burning series it may be concluded that it was not mix D+E+Bx produced by adding a flux (Bx = bauxite) that was easiest to burn, but mix A, which did not contain any admixture at all. With the latter, free lime disappeared at 2460 deg. F. almost entirely under the given time conditions; the free lime quantity showed at 2280 deg. F. a more advanced reaction compared with the other two samples. The quality of the clinkers sharply burned at the latest stage was the same, as was anticipated, with equal chemical compositions. An exception was the heat evolution during hardening, which was higher at D+E+Bx.

The experiments prove that the raw material constituents of the mixes B+C and D+E+Bx were less reactive at the lower burning stages than A.

TABLE 5.—CHEMICAL COMPOSITION OF CLINKERS BURNED FROM RAW MIXES A, B+C, D+E+Bx AT DIFFERENT TEMPERATURES IN THE LABORATORY FURNACE.

Clinker burned from							Free lime content at burn. Temp. F°					Potential Compound Composition of Clinkers burned at 2560/2,					Heat of Solution of Clinkers burned at: (Calories/gr.)		
Raw mix	Ign.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	2280/5	2370/5	2460/5	2500/5	2560/2,	C_3S	C_2S	C_3A	C_2A_1	C_4AF	2460/5	2500/5	2560/2,
A	0.30	22.54	5.62	2.91	66.62	1.97	6.2	1.8	0.6	0.1	0	60.5	19.3	8.3	1.5	9.0	643	617	640
B+C	0.32	22.80	5.26	3.46	66.62	1.51	9	3	1.7	1.1	0.2	57.7	22.1	8.0	0	10.7	650	640	639
D+E +Bx	0.50	22.72	5.52	2.89	66.66	1.56	8.3	3.4	1.1	0.7	0.15	59.4	20.4	8.2	1.3	9.0	649	629	637

TABLE 6.—PROPERTIES OF CEMENTS BURNED FROM RAW MIXES OF THE SAME CHEMICAL COMPOSITION BUT OF DIFFERENT RAW CONSTITUENTS.

Burned from	Weight per litre	Setting Time water	Init.	Final	Soundness Lechatelier	Bending strength (11% water) plastic consistency 7 days	28 d. water	28 d. comb.	Crushing strength (8% water) earth moist consistency 7 days	28 d. water	28 d comb.
A	1115 gr.	26.4%	3:50	5:15	0.5 mm.	632 lbs./in.²	673 lbs./in.²	930 lbs./in.²	4860 lbs./in.²	8260 lbs./in.²	8260 lbs/in.²
B+C	1120 gr.	26.2%	3:10	4:30	2.0 mm.	542 lbs./in.²	665 lbs./in.²	714 lbs./in.²	4140 lbs./in.²	7100 lbs./in.²	7140 lbs./in.²
D+E +Bx	1110 gr.	26.3%	3:40	5:15	1.0 mm.	551 lbs./in.²	667 lbs./in.²	782 lbs./in.²	4800 lbs./in.²	8350 lbs./in.²	8280 lbs./in.²
A	1115 gr.	26%	5:00	5:45	0 mm.	583 lbs./in.²	716 lbs./in.²	830 lbs./in.²	5530 lbs./in.²	8260 lbs./in.²	8850 lbs./in.²
B+C	1110 gr.	26%	4:00	5:45	0.5 mm.	546 lbs./in.²	665 lbs./in.²	796 lbs./in.²	4060 lbs./in.²	7660 lbs./in.²	7760 lbs./in.²
D+E +Bx	1120 gr.	26.2%	4:30	5:30	15 mm.	595 lbs./in.²	716 lbs/in.²	764 lbs./in.²	5380 lbs./in.²	7370 lbs./in.²	7800 lbs./in.²

* Inner surface area for all mixes was 2000 sq. cm. per gram, plus or minus 10 sq. cm. per gram. Burning temperature of first group of raw mixes was 2500/2 and for second group, 2560/2.

The fact was also striking that in all trial burnings, mixes of the composition A retained their forms despite great shrinkage of volume during the evaporation of water, dissociation of carbonates, and sintering, while the other samples burned from B, C, D and E were full of flaws which sometimes stood ½ in. apart.

For several months an opportunity presented itself of observing simultaneously the raw material types B + C in a battery of six shaft kilns, and the same opportunity was also given in an oil-fired rotary kiln of the same plant. The latter, worked on the thick-slurry method, was 335 ft. in length, with 10-ft. dia. enlarged burning zone and heat exchange chains at the feed end. Exhaust gases were drawn with a motor-driven louvre damper having automatic draft control. The fuel used had a calorific value of 19,800 B.T.U. per lb. and practically no ash

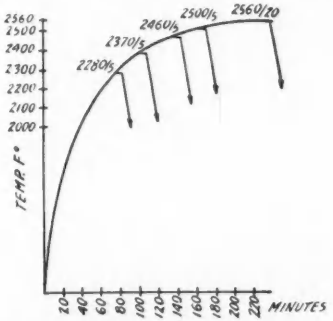


Fig. 3.—Progress of Heating Raw Mix in the Laboratory Furnace.

content. The raw material mixture was ground to thick slurry in a 4-compartment wet mill 7-ft. dia. and 33-ft. long and blended in slurry storage bins to the desired chemical composition to a high degree of precision.

Rotary versus Shaft Kilns.

The burning with B+C in the rotary kiln was entirely uniform. The coating of the kiln lining which, after starting the kiln, was burned on to the burning zone held up exceedingly well, so that it was possible to work with clay firebricks in the burning zone for almost two years at maximum kiln capacity. Owing to the comparatively small quantity of water required for the thick slurry consistency, heat economy was favourable.

Shaft kilns worked less successfully with the same material, the cost of production being higher than with the rotary kiln due to the larger labour requirements and relatively smaller capacity. Clinker quality was inferior to that produced by the rotary kiln. The maximum lime saturation value which could be maintained while keeping good soundness was about 91 per cent.

The comparison between the two kiln systems, however, gave quite different results when raw material of the type (A) was used. Burning in the rotary kiln only showed a difference compared with the raw material combination B+C, the

material requiring more water to obtain the necessary thick slurry consistency. In the case of shaft kilns, however, a particular improvement could be observed. Burning became more uniform, the efficiency of the kilns was considerably raised, and the quality of the clinker equalled that burned by the rotary kiln. Thus, by showing its actual behaviour in automatic shaft kilns, the great importance of raw material (A) could be proved (*Table 7*). It became possible to operate at maximum capacity with a heat consumption of 650,000 B.T.U. per barrel of clinker. The maximum lime saturation value at which good soundness could be held

TABLE 7.—AVERAGE RESULTS OBTAINED BY USING DIFFERENT RAW MATERIAL CONSTITUENTS.

	Shaft Kiln Plant Raw mix consisting of		Rotary Kiln Plant Raw mix consisting of	
	A	B+C	A	B+C
	briquettes ("earth moist" cons)		Thick Slurry	
Water (in %) required for:	16	14.5	48	42
Fuel consumption B.t.u./bbl. Cement	650,000	920,000	1,150,000	1,050,00
Cement fineness: Spec. surface area weight per	approx. 1800 cm.²/gr. in all cases			
litre in grams	1010	990	1025	1015
Setting time:				
Water used for plastic consistency	25.6%	26.2%	25.6%	25.6%
Initial set at 65° F	150 min.	120 min.	150 min.	150 min.
Final set at 65° F	230 min.	210 min.	210 min.	210 min.
Soundness:				
Lechatelier test in m/m free	0	1.5	0	0
CaO in Clinker	0.2%	1.8%	0%	0%
Tensile strength acc. to B.st. Specif. lbs/in²				
3 days	520	450	510	525
7 days	615	470	625	610
Crushing strength mortar with 8% water, lbs./in² ("earth moist" cons.)				
3 days	5460	4260	5530	5670
7 days	7080	5690	7440	7440
28 days water st.	9360	6950	9790	9560
28 days comb. st.	9780	8000	10050	10100
Bending strength mortar with 11% water, lbs/in² (plastic cons.)				
3 days	596	468	582	596
7 days	736	624	695	723
28 days water st.	908	822	908	886
28 days comb. st.	994	914	1002	990

was 97 per cent. Nearly the same satisfactory results could be obtained in the shaft kilns if, beside (A), the raw constituents (D) and (E) were mixed with a certain amount of iron oxide to keep the silica modulus normal. When, however, the content of (A) in the raw mix fell below 70 per cent., difficulties in the shaft kilns recurred.

Thus, practical experience corroborated to a high degree the results obtained in the laboratory. The rotary kiln was not sensitive to various raw material combinations of equal chemical composition, except some trifling fluctuations

in heat consumption due to different water content in the slurry. Material (D) tended to form dust rings following the heat exchange chains, but experience was too short to pass a definite opinion in the matter.

Shaft kilns, on the other hand, were very sensitive to variations of raw constituents; with certain kinds of materials burning was difficult and expensive, but with other types it was unusually favourable. The special burning advantages of such materials could be used in shaft kilns so profitably that the larger number of men employed and other circumstances involving additional expenditure of the shaft kiln process could be more than compensated. The quality of the burned clinker was uniform, and represented the limit that could be reached on the basis of the given chemical composition.

The difference in the behaviour of raw materials of different physico-chemical state was therefore of great importance in practice. It must also be pointed out that the raw mix was expected to meet various requirements which were different when various kiln systems were in operation. In the case of shaft kilns, the briquettes had to be of good resistance to wear lest they should crumble when fed into the kiln. They must acquire high porosity and good strength in the calcining zone to allow the water and CO_2 to leave easily and to effect thorough burning without difficulties. With the rotary kiln, the raw mix had not to consume too much water for the slurry; the dehydrated and partially calcined material should not dust but must form balls of good mechanical resistance. The ability to burn a good coating on the lining is influenced both by the properties of the raw mix and the quality of firebricks used in the burning zone.

Plasticity and Adsorption of Raw Materials.

Plasticity can be defined as a group of properties which are ascertained by well-known physical and colloid-chemical principles.[11] Clay, which is made plastic by means of water, represents a system of capillaries which the liquid enters, in consequence of which swelling, adhesion, and internal friction play a distinct part in the development of plasticity.[12] In considering adsorption phenomena, the type of adsorbing surface (shape of the particles) and the degree of comminution are of great importance. Adsorption can vary between cases where the external surface of particles or that of the pores and capillaries are concerned. This makes us realise that grinding to the same fineness does not always lead to the same plasticity when the raw mixes are composed of constituents with different physical or colloid-chemical properties. Allophane clays[13] consist of fine crystalline and gel particles, their degree of dispersion being higher than that of purely crystalline Kaolinits, feldspar-clays, etc.[14] On the other hand, small differences in fineness of grinding are insignificant for the behaviour of the raw mix, provided the same types of raw constituents are used.[15] Extremely fine grinding, however, does not improve the plasticity of the raw mix. On the contrary, it can very often be found that an advantageous plasticity disappears when the material is ground too finely. (See also *Fig.* 5). Similar behaviour was found by investigators in the case of Kaolin, which was accounted for by the fact

that the plate-shape of the particles so important to Kaolin-plasticity was destroyed by very fine grinding.([16])

At the dehydration of the clay-constituent heat absorption usually takes place at 900 to 950 deg. F., and heat evolution at 1,700 to 1,800 deg. F. The discharging of water as well as the changes in internal structure resulting therefrom([17]) are of great importance for burning in various kiln systems. Burning experiments in the laboratory furnace revealed differences in the behaviour of raw mixes of the same chemical composition. In these tests, however, the plasticity of the various samples had not the same importance that they have in different kiln systems in service. Observations in different plants proved that raw mixes of the same chemical composition but of different physico-chemical state (usually incorrectly referred to as " plasticity ") greatly affected manufacturing costs and cement quality. The constituents which can be considered " easy to burn " exhibited a pronounced difference from other materials as to their plasticity.

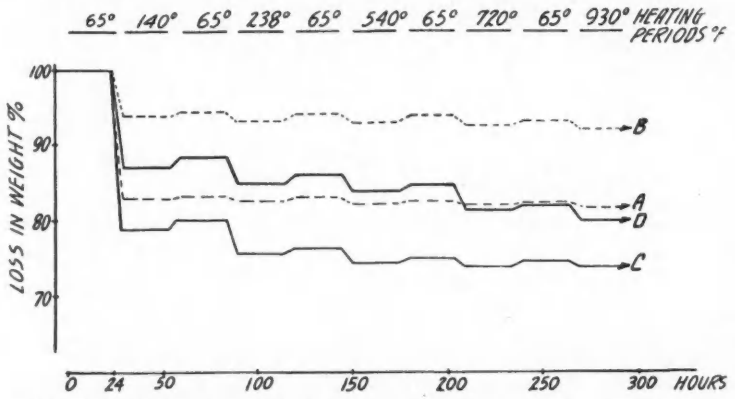


Fig. 4.—Dehydration of Various Raw Mix Constituents at Different Temperatures.

Thus the necessity arose to perform in the laboratory a series of practical " plasticity " examinations which were adjusted to the particular circumstances in the plants—the ability to absorb water and discharge it at various temperatures, the strength of dried raw masses as well as their resistance to mechanical action (wear), and the practical fineness—all of which were of special interest for each raw material.

Tests were conducted in the following way. Each constituent was dried and ground to 80 per cent. minus the 170-mesh sieve and prepared to equal " earth-moist " consistency with an adequate quantity of water in moulds, which were similar to those used for tensile strength briquettes. Then the samples were systematically exposed to gradual heating to different temperatures and the losses in weight determined. Each heating period lasted for 24 hours, then the samples were cooled off to 65 deg. F. and left at this temperature for

24 hours. Then the next heating stage started again (*Fig.* 4). The results demonstrate that the water consumption required to obtain the same earth-moist consistency was the highest for the constituent (C) and the smallest for (B). The dehydration proceeded slower with (A) than with all other constituents. Grinding in the laboratory mill resulted for all samples in 98.8 per cent. minus 72 mesh, 82 per cent. minus 170 mesh, and 55.0 per cent. minus 50 microns (determined with an air-elutriator). After heating was finished up to 930 deg. F., tensile strengths were tested. Results (in lb. per sq. in.) were as follows: A, 110; B, 50; C, was full of flaws, could not be tested; D, 30; E, 10. The same strengths were also reached by heating the samples to 930 deg. F. without any interruptions. The raw-constituent (A) which was most favourable in shaft kilns, gave the highest strength, its water-requirement for wet process slurry also being highest (48 per cent.). Plant mill grinding, which was somewhat coarser than laboratory-grinding, proved that (A) produced still higher strength when moulded to briquettes and heated to 930 deg. F. Laboratory grinding

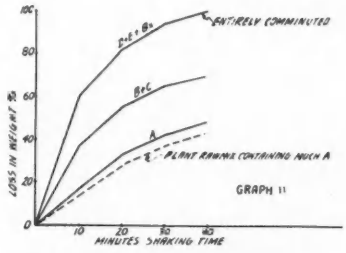


Fig. 5.—Resistance of Different Raw Mixes against Wear.

produced 37 per cent. of particles of "medium" size (50 to 88 microns), whereas plant-grinding had 50 per cent. of the same particle size-class. (Investigated with the Andreasen pipette-apparatus.)

Wear Tests.

A method was adopted to examine the resistance against wear of heated balls formed from the different raw mixes. These were prepared with about 20 per cent. of water, and dried at 140 deg. F. for 24 hours. The wear test was carried out in a sieving machine. After being shaken for definite periods, the balls were rubbed in different ways, varying with the physico-chemical state of the sample. By determining the losses in weight after definite periods of shaking, curves were obtained which are typical of the resistance to mechanical friction. Repeated experiments showed very slight differences in the values obtained (*Fig.* 5). The wear tests also confirmed the results established by the heating experiments. Here again it was not the highest degree of fineness at which the greatest resistance was displayed. With somewhat coarser distribution of

particles, in which the " medium size " (50 to 88 microns) seems to be a matter of some importance, the lowest wear figures were obtained.

When raw materials of different hardness or brittleness are ground, certain constituents (SiO_2, $CaCO_3$) may remain in a somewhat coarse form. For example, when grinding a mix of soft chalk and hard flint for the purpose of obtaining a favourable silica modulus, an accumulation of SiO_2 in the residue of 170 mesh will be found. On grinding a particularly hard limestone with soft clay, $CaCO_3$ may accumulate in the same way. This peculiarity is usually observed when compound mills are in operation and can partly be counteracted by grinding in closed circuit.

TABLE 8.—INFLUENCE OF GRAIN DISTRIBUTION IN RAW MIX ON BURNING IN THE LABORATORY FURNACE.

The raw mix was composed of the raw constituents = C + D + E + Ash

Sample (1) (all constituents were mixed and ground in the laboratory mill)
Sample (2) (each constituent was ground separately and then mixed)

Fineness of the raw mixes:

	minus 72 mesh %	minus 170 mesh %	Residue on Sieve 170 mesh	
			$CaCO_3$ content %	SiO_2 content %
1	96	84.5	78.25	13.5
2	94.8	86	67.75	26.4

Fineness of Clinkers burned at 2370/s and ground in the laboratory mill:

	minus 170 mesh	minus 200 mesh	weight per litre
1	93.5	81.5	1055 gr.
2	93.3	82	1060 gr.

Properties of Cements

	Setting time			Soundness	Bending strength plast. consistency 11% water			Crushing strength earth moist consistency 8% water		
	water	Init	Final	le Chatelier	7 days	28 d. water	28 d. comb.	7 days	28 d. water	28 d. comb.
1	26.5	155′	225′	2 mm	540	632	725	4880	7790	8300
2	26,5	155′	245′	1 mm	544	628	740	4925	8210	8415

In order to determine the influence of such heterogeneity on burning, the same raw constituents, chalk and flint, to which clay and some ash were added to reach a normal chemical composition with a lime-saturation value of 94, were ground in the laboratory mill, first together (raw mix No. 1), then separately (raw mix No. 2) to 80 per cent. minus on 170 mesh (*Table* 8). In this way a different particle distribution was effected with the same chemical composition, as the harder constituent, flint, was coarser after the common grinding of the charge; i.e., the residue on 170 mesh accumulated some SiO_2. When the raw mix was

prepared after each constituent was ground separately, this accumulation could almost be eliminated.

Tests in the laboratory furnace proved that the burning-temperature of 2,370 deg. F. which lasted only five minutes was sufficient to produce clinker of equal quality from both raw mixes. Thus, SiO_2 particles greater than 88 microns could be brought into reaction without difficulty. That this not only comprised "a reaction of all SiO_2," but also the formation of the desired clinker constituents, was also proved by the quality of the burnt clinkers ground in the laboratory mill to the same degrees of fineness. Silica particles up to 200 microns reacted almost completely at $2{,}500/_5$—up to 500 microns at $2{,}560/_{20}$. With the latter burnings, however, free lime did not entirely disappear, more $2CaO.SiO_2$ was formed, and the clinkers dusted (i.e. crumbled) on storing. When still larger SiO_2 grains (up to 800 microns) were in the mix, after burning white dots remained in the clinker, from which dusting started. Such large flint lumps could only be brought into reaction by changing the chemical composition (reducing the lime-saturation value from 94 to 87).

The possibility of sintering coarser raw constituents is strongly influenced by their physico-chemical state. This was clearly observed on burning in the shaft kiln battery. With a higher percentage of raw material (A) in the raw mix, faultless clinker could be obtained, in spite of coarser raw material grinding, kiln capacity remaining almost unchanged. Somewhat higher silica modulus and lime-saturation value could also be tolerated without difficulty. With the raw constituents (D), (E) and (C) burning reacted on coarser grinding much more sensitively. With higher silica modulus burning was rendered very difficult, and with higher lime-saturation value soundness also became deficient. However, with flux-admixture of Fe_2O_3, by which silica modulus and lime-saturation value were both lowered, burning became quite faultless.

The coarser grains in the raw material mixture, though slackening the rate of reaction at heating, do not always prove to be a disadvantage when kiln systems are used where the raw mix is fed in the form of briquettes. Apart from the fact that certain particle-distributions favour plasticity, coarser grains in the calcining zone seem to facilitate the passage of combustion air through the briquettes, thereby securing more uniform sintering. Experience has shown that in shaft kilns with somewhat coarser anthracite or coke-dust, better results were obtained than by adding finely ground coal. It is also remarkable that adding moderately granulated clinker-dust to the raw mix can greatly promote burning in automatic shaft kilns. In the case of certain raw materials it has become possible to increase greatly the kiln capacity and to improve fuel economy with unaltered cement quality by circulating 5 per cent. to 10 per cent. clinker dust with the raw mix. (The author is indebted to Mr. E. W. Ruhnow for his assistance.)

BIBLIOGRAPHY.

[1, 2, 3] Rankin, G. A., and Wright, F. E., *Amer. J. Sci.*, (4) 139 (1915); Hansen, W. C., Brownmiller, L. T., and Bogue, R. H., *J. Amer. Chem. Soc.*, 48, 1261 (1926); Lea, F. M., and Parker, T. W., *Phil. Trans. Roy. Soc.* (London), Series A, 234, No. 731 (1934); Lea, F. M., and Parker, T. W., *Build. Res. Tech. Paper*, No. 16 (1935); Yamauchi, *J. Jap. Ceram. Assn.*,

46 (1938); Insley-McMurdie, U.S. Bur. of Standards, Res. Paper No. 1074; Taylor, *Cem. & Lime Manuf.*, p. 247, 1938; Shipman, *Pit & Quarry*, July, 1936—Feb., 1937; Dahl, L. A., *Rock Products*, Sept., 1938—April, 1939; Bogue, R. H., *Cem. & Lime Manuf.*, Oct., 1939—Jan., 1940.

[4] Tammann, *Z. f. anorg. Chem.*, 107 (1919).

[5] Jander, *Z. f. angew. Chem.*, 686 (1938).

[6] Flint, E. P., *Rock Products*, October, 1939, p. 40.

[7] Eitel, W., *Phys. Chemie der Silicate*, 1929.

[8] Eitel, W., *Zement*, 30, 455–459, 649–672 (1938).

[9] Blank, A. J., *Rock Products*, May–Sept., 1938, and Koyanagi, K., *Rock Products*, May 10, 1930, p. 82.

[10] Gottlieb, *Cem. & Lime Manuf.*, March, 1940.

[11] Salmang & Becker, *Sprechsaal*, 59, 1926.

[12] Immke & Kratzert, *Tonind. Ztg.* 51, 1927. Semjatschensky, *Transact. Ceram. Res.*, Moscow, No. 7, 1927.

[13] van Bemmeleen, *Z. f. anorg. Chem.* 66, 1910.

[14] Alexander, *J. Amer. Ceram. Soc.* 1925 (3). Rinne, *Z. f. Kryst.* 60, 1924.

[15] Steiner, *Zement*, p. 469, 1935.

[16] Le Chatelier, *La Cilice et les Silicates*, 1914. Salmang, *Z. f. anorg. Chem.* 162, 1927.

[17] Spangenberg & I. Rhode, *Keram. Rundschau* 35, 1927. Neumann & Kober, *Sprechsaal*, 59, 1926. Kozu & Masuda, *Sci. Rep. Tohoku Imper. Univers.* Sendai Ser. III, No. 1, 1926.

Cement in the Form of Pellets.

According to a recent number of *Rock Products*, a Portland cement in the form of small pellets or granules which disintegrate into cement particles when added to water has been patented by Mr. Ira C. Bechtold, and the patent has been assigned to the California Portland Cement Co., of Los Angeles. The cement particles are conglomerated into small pellets by blowing the finely ground cement upward in a "shot tower." From the top of this tower small globules of soap or resin are sprayed, and the cement particles as they rise upward collect on and stick to the globules as they fall through the tower and are carried to a dryer. Here the cement particles, on drying, are held together into free-flowing pellets. The resin or soap holding the particles together in the pellet readily disintegrates when the pellet-cement is mixed with water. The principal claim made for cement supplied in this form is the absence of dusting when it is used.

SUPER REFRACTORIES for CEMENT KILNS

ALITE No. 1. 68% ALUMINA
Refractory Standard 3260° Fahr.
ALITE B. 57% ALUMINA
Refractory Standard 3180° Fahr.
ALITE D. 41% ALUMINA
Refractory Standard 3150° Fahr.

E. J. & J. PEARSON, LTD.,
STOURBRIDGE, ENG.